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Anionic Synthesis of Narrow Molecular Weight Distribution Poly(trimethylvinylsilane) (PTMVS), Polystyrene−PTMVS Block Copolymers, and Poly(phenyldimethylvinylsilane). Conversion of Poly(phenyldimethylvinylsilane) into Poly(fluorodimethylvinylsilane)

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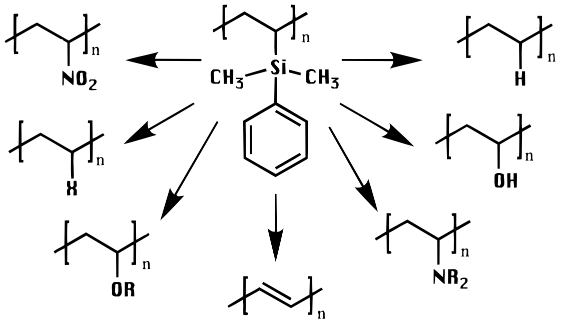
ABSTRACT: The anionic polymerizations of trimethylvinylsilane (TMVS) initiated by *t*-BuLi in toluene at −20 °C and of phenyldimethylvinylsilane (PDMVS) at 0−20 °C proceed in high yields (>95%), giving narrow molecular weight distribution (MWD ≤ 1.15) polymers. Polystyrene−PTMVS AB block copolymers having relatively narrow molecular weight distributions were synthesized by initiation of TMVS by poly(styryllithium). The reaction of poly(phenyldimethylvinylsilane) (PPDMVS) with $HBF_4 \cdot Et_2O$ in toluene at 60 °C resulted in the formation of poly(fluorodimethylvinylsilane) (PFDMVS) as shown by ^{1}H and ^{19}F NMR.

Introduction

Poly(trimethylvinylsilane) (PTMVS) and poly(phenyldimethylvinylsilane) (PPDMVS), their copolymers, and their polymer blends have been demonstrated to possess excellent transparency, flexibility, permeability, and heat resistance and have been widely applied and studied as materials for gas-separation membranes,[1−3] optical fibers,[4] contact lenses,[5,6] coating of waterproofing fabrics,[7] optical disks,[8] photoresists,[9] etc. PTMVS and PPDMVS might also be useful as intermediates in the synthesis of monodisperse polyethylene, poly(vinyl alcohol), poly(vinyl ether), polyacetylene, poly(vinyl halide), poly(nitroethylene), and poly(vinylamine) (Scheme 1). Furthermore, PTMVS- or PPDMVS-containing block copolymers might be converted to a series of novel block copolymers. However, such reactions of PTMVS and PPDMVS have not been explored. Hence, the synthesis of narrow MWD polymers and block copolymers of PTMVS and PPDMVS would be of interest.

Scheme 1. Unexplored Reactions of PPDMVS



Silicon stabilizes adjacent carbanions by overlap with its vacant d orbitals.[10] Vinylsilanes such as TMVS and PDMVS are therefore possible candidates for "living" anionic polymerizations. The anionic polymerization of TMVS and PDMVS initiated with alkyllithiums was first reported by N. S. Nametkin et al.[11] They synthesized homopolymers,[11] block polymers,[12] and graft copolymers[13] under vacuum or argon atmosphere at temperatures above 0 °C up to 70 °C (mostly 35−40 °C) for 18−300 h, by using butyllithiums, ethyllithium, and metallic lithium as initiators and benzene, toluene, cyclohexane, and heptane as solvents. These polymers were characterized by ^{1}H and ^{13}C NMR,[14] DSC[15], and viscometry.[16] Since the polymerization of PTMVS and PPDMVS is slow at low temperatures, higher reaction temperatures (25−60 °C) were chosen to produce somewhat polydisperse polymers ($D \sim 1.3$) in quantitative

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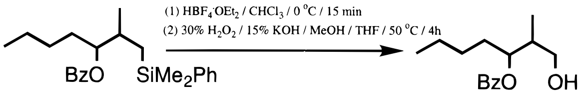
Scheme 2. Synthesis of an Alcohol via Oxidative Cleavage of the C−Si Bond Reported by Tamao



yields (96%). The somewhat broader polydispersity of these polymers was believed to be due to self-termination of the living chains, resulting from hydride elimination. Later studies by Rickle[17,18] confirmed such side reactions and their effects on MWD and yield, especially for high molecular weight PTMVS. He also found that such side reactions were enhanced by the addition of ethers.[18] More recently, the anionic polymerizations of dimethylphenylvinylsilane,[19] allyldimethylvinylsilane,[20] diallylmethylvinylsilane,[20] and allylmethylphenylvinylsilane[20] were reported. The latter investigation demonstrated the formation of narrow molecular weight distributions.

We now wish to report the synthesis of narrow MWD PTMVS and PPDMVS by anionic polymerization of the corresponding vinyl monomers and their attempted transformation into other polymers (Scheme 1). In order to minimize the termination reactions and obtain better molecular weight distribution samples, we tried various solvent systems at lower temperatures (below 0 °C) for relatively long reaction times. High-vacuum (10^{-6} Torr) conditions and ultrapure solvents and monomers were employed.

Protodesilylation and oxidation of various organosilicon compounds have been developed by Tamao,[21−23] Fleming,[24,25] and Nishiyama.[26] A variety of alcohols could be synthesized in this way, especially by oxidative cleavage of "unactivated" alkyl−silicon bonds, using the phenyldimethylsilyl group as a masked hydroxyl group. In these procedures, phenyl−silicon bonds are cleaved by acids (tetrafluoroboric acid−diethyl ether complex) prior to oxidation (Scheme 2). Protodesilylation of the phenyl group converted each of the silanes into the fluorosilanes, which further reacted with excess of *m*-chloroperbenzoic acid (MCPBA) or 30% hydrogen peroxide to give the corresponding alcohols. However, it was not possible to remove trimethylsilyl groups except under the most vigorous conditions, such as concentrated sulfuric acid. Even in this case, only partial methyl cleavage was possible.[24]

However, none of these reactions involved polymers. A successful transformation of a compound with a structure similar to that of PPDMVS was reported by Tamao and co-workers (Scheme 2).[22] Thus, the synthesis of poly(vinyl alcohol) by this route may be possible.

Experimental Section

Materials. TMVS was purchased from Huls America Inc. PDMVS was synthesized by adding vinyldimethylchlorosilane (Huels America Inc.) dropwise to a phenylmagnesium bromide/THF solution at −20 °C followed by reflux for 2.5 h. Fractional distillation gave over 70% isolated yield of product (bp 75−79 °C/10 mmHg). The PDMVS was characterized by ^{1}H NMR and GC−MS. Both TMVS and PDMVS were distilled from CaH_2 twice and once from a potassium mirror under high vacuum to eliminate moisture and other impurities. The monomers were stored in evacuated ampules at −20 °C. Toluene was purified by stirring over fresh K−Na alloy under vacuum overnight. Tetrafluoroboric acid−diethyl ether complex (85%) (Aldrich) was used as received.

Polymerizations. Anionic polymerization was carried out by initiation of purified TMVS and PDMVS with *n*-, *sec*-, or *tert*-butyllithium in toluene and toluene−THF mixtures at −70 to 40 °C. Reactions took 12 h to several days and were terminated with MeOH followed by precipitation in cold MeOH. Polystyrene-*b*-TMVS block copolymers were synthesized via a similar procedure. A small fraction of the polystyryl anion intermediate was protonated and analyzed by SEC. The polymers and copolymers were characterized by SEC and by ^{1}H and ^{13}C NMR (250 MHz).

Table 1. Anionic Synthesis of PDMVS in Toluene Initiated with *t*-BuLi[g]

entry	temp/time (°C/h)	M_n(calc)	M_p[a]	MWD[b]	yield[c] (%)
1	−25/24	41000	(no polymer)		0
2[d]	−25/12	12900	14200	1.40	>98
3	0/23	21000	(oligomers)		
4[e]	−20/14	5900	400−1000	1.20	3
5	40/2	4100	3200	1.46	80
6	20/24	4500	4200	1.23	75
7[f]	0−20/44−72	8000	7400	1.12	>94

[a] SEC peak molecular weight (M_p). [b] MWD = M_w/M_n. [c] Isolated yield. [d] Bulk polymerization. [e] 10% (v/v) THF was added to toluene as cosolvent. [f] Two days at 0 °C and three days at 20 °C. [g] Monomer concentration is 1.3 M.

Protodesilylation Reactions. Plastic vessels were utilized during the protodesilylation to avoid the reaction between $HBF_4{\cdot}OEt_2$ and glass. In order to obtain reproducible and quantitative conversions, low MW-PPDMVS samples with identical degrees of polymerization (DP = 46) were used in all cases. The reaction of PPDMVS with $HBF_4{\cdot}Et_2O$ was carried out in a polypropylene vessel. Purified PPDMVS (DP = 46) was dissolved in chloroform, and $HBF_4{\cdot}Et_2O$ was then added to the PPDMVS solution (1.0 g in 15 mL) under argon. The reaction mixture was stirred at 60 °C for 3 h. During this protodesilylation process, the reaction temperature was carefully monitored in order to prevent boiling of the solvent and swelling of the plastic vessel. After evaporation of the volatile materials, the resulting fluorosilane polymer was purified by reprecipitation in cold methanol and was characterized by ^{1}H and ^{19}F NMR and by SEC.

Oxidation Reactions. The PFDMVS obtained (0.57 g) was dissolved in 30 mL of THF and transferred to a glass flask. A solution of 1.45 g of KOH in 20 mL of MeOH was introduced into the reaction vessel followed by the dropwise addition of 14 mL of 30% H_2O_2 aqueous solution. The reaction mixture was refluxed (50 °C) for 4−19 h. The resulting polymer was not water soluble, indicating that conversion was incomplete. The use of dioxane instead of THF/MeOH as solvent following the same reaction procedure was also unsuccessful. The use of 3 equiv of *m*-chloroperbenzoic acid instead of H_2O did not result in the formation of the desired polymer.

Characterization. Molecular weight and molecular weight distributions were obtained by SEC using a Waters 510 HPLC equipped with a Model 410 refractive index detector, a Model 484 UV absorbance detector, a liquid flow meter, and a Zenith PC interface for data collection. A set of two Waters Ultramicrostyragel columns was used with pore sizes of 500 and 10 000 Å. The linear range of separation was between MWs of 500 and 500 000. The columns were thermostated at 35.0° by a column oven. The elution solvent was THF and the flow rate was monitored by a flowmeter and kept at 1.0 mL/min. Polystyrene standards (Polysciences) were used to calibrate the system. Molecular weights as determined by this method were reproducible to within 3−5%. Proton NMR measurements were performed in $CDCl_3$ on a Bruker 25 MHz FT-NMR. Fluorine-19 measurements were carried out on a Bruker AM 360 in deuteriochloroform, using $CFCl_3$ as internal standard.

Results and Discussion

Polymerization. The polymerization of PDMVS (1.3 M) was carried out in toluene at various temperatures using *t*-BuLi as initiator (Table 1). At −25 °C, the polymerization was too slow to produce polymers, and most of the monomer was recovered after 24 h. The bulk polymerization at −25 °C for 12 h was more

Table 2. Anionic Synthesis of Poly(trimethylvinylsilane) (PTMVS) and Polystyrene-*b*-PTMVS (PS-*b*-PTMVS) Copolymers in Toluene Using *t*-BuLi as Initiator

no.	temp/time (°C/h)	M_n(calc)	M_p[a]	MWD[b]	yield[c] (%)	PS (%)[d]
1	−78/96	17000				
2	−10/1	16000	2600	1.10	6	
3	0−2/20	20000	23400	1.56	90	
4	−20/96	13000	10000	1.10	82	
5[e]	20/83	8800	6800	1.10	56	83%
6[f]	−20/96	25100	22000	1.18	80	57%

[a] SEC peak molecular weight (M_p). [b] MWD = M_w/M_n. [c] Isolated yield of PTMV. [d] Polystyrene-content measured by NMR. Agreement with SEC values is within 5%. [e] In cyclohexane containing 2% (v/v) THF. [f] The SEC M_n of the polystyrene precursor block is 12500.

successful, giving PDMVS in quantitative yield. The MWD was not very narrow however ($M_w/M_n = 1.4$).

The polymerization at 0 °C produced only oligomers (MW = 400−1000) after 23 h. Polymerization at −20 °C in the presence of 10% (v/v) THF in toluene after 14 h, resulted likewise in low isolated yields (3%) of oligomers (MW = 400−1000). It has been shown previously that addition of a trace amount of THF increased the propagation rate but chain termination as well.[25] On the other hand, at higher temperature (40 °C), PPDMVS was obtained in high isolated yield (80%) after 2 h. SEC analysis showed a broadened (D = 1.46) MWD, which may due to increased termination at this temperature. A better MWD (=1.23) PPDMVS was produced in good yield (75%) by using a lower reaction temperature (20 °C) and longer reaction time (24 h).

The best results were obtained when PDMVS was polymerized at 0 °C for 2 days followed by raising the temperature to 20 °C for another 3 days. In this case, the MWD of the polymer was 1.12 (MW = 7400) and the yield was nearly quantitative (Table 1).

For the case of the polymerization of TMVS initiated with *t*-BuLi in toluene at −78 °C, no polymerization occurred even after 4 days. At −10 °C after 1 h, only low-MW oligomers (MW = 2600) were formed in low yields (6%). However, at a higher temperature (0−2 °C), TMVS could be polymerized quantitatively in 20 h, producing however PTMVS with a broad MWD (=1.56). Better results were obtained at −20 °C in toluene for 4 days, which produced high yield (>80%) and narrow MWD (=1.1) (MW = 10000).

The use of *n*- or *sec*-butyllithium instead of *t*-BuLi gave similar results. For the case of "living" polystyrene as initiator, the orange color of the PS anion instantly turned yellowish upon addition of TMVS, indicating rapid initiation. Controlled block lengths of polystyrene and PTMVS could be obtained by controlling the respective monomerpinitiator ratios. The PS-*b*-PTMVS copolymers were synthesized with a PS content ranging from 57 to 83%, with molecular weights ranging from 6800 to 22000. Number-average molecular weights were determined by proton NMR and by SEC. Thus a small fraction of the polystyryl anion precursor block was protonated and analyzed by SEC. Integration of the proton NMR spectrum of the block copolymer then gave the mass of the second block. Interestingly, the block copolymer molecular weights obtained in this way agreed to within 5% with the SEC values (Table 2). This indicated that, at least for PTMVS, the use of polystyrene standards did not lead to significant errors in the molecular weight of PTMVS. Although similar PS−PPDMVS block copolymers were not synthesized to check this, the similarity of PTMVS and PPDMVS makes it plausible that the use of polystyrene standards gives at least an order of magnitude for the PPDMVS molecular weights.

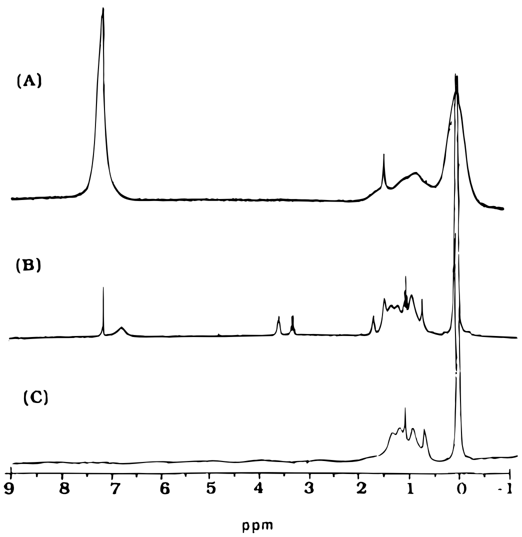


Figure 1. Proton NMR spectra in $CDCl_3$: (A) PPDMVS; (B) product after protodesilylation at 40 °C; (C) product after protodesilylation at 60 °C (PFDMVS).

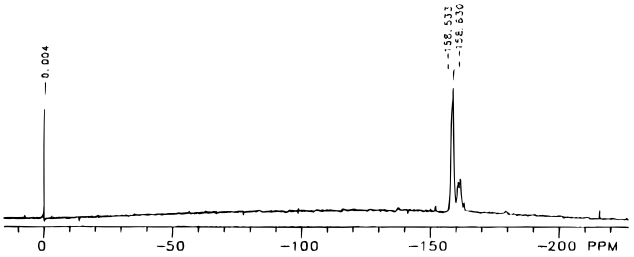


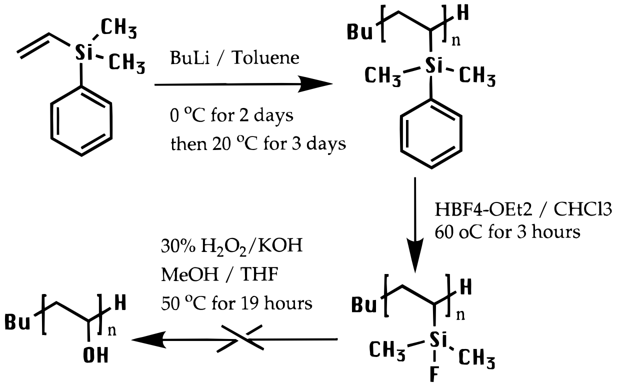
Figure 2. Fluorine-19 NMR spectrum in $CDCl_3$ of PFDMVS using $CFCl_3$ as internal reference (δ = 0.00).

Cyclohexane containing 2% (v/v) THF was also found to be a good solvent system for the polymerizations of TMVS and for the synthesis of PS-*b*-TMVS. However, the high freezing point (6.5 °C) of cyclohexane limited its use to ambient temperatures.

Protodesilylation. The protodesilylation of PPDMVS (6.7 wt %) in $CHCl_3$ carried out by using $HBF_4 \cdot OEt_2$ (85%) at 0 °C for 15 min similar to that used for organosilicon compounds[27] was unsuccessful, and the starting material was recovered quantitatively. At 20 °C after 3 h, a white powder was obtained after removal of excess reactants and solvent. The polymer was redissolved in THF and purified by reprecipitation in cold methanol. Proton NMR integration showed 50% substitution of phenyl by fluorine. At 40 °C, after 3. 5 h, 90% substitution was obtained, and an essentially quantitative substitution was obtained at 60 °C for 3 h. The ^{1}H NMR of the product is shown in Figure 1. The spectrum exhibited the documented structure of poly(fluorodimethylvinylsilane) (PFDMVS) (δ = 0.1, doublet, 6H, $Si(CH_3)_2$; δ = 1.1, multiplet, 3H, CH_2CH) and phenyl absorptions were now absent.

Fluorine-19 NMR confirmed the structure of the dimethylfluorosilyl group (Figure 2), showing a strong absorption at −158.6 ppm. A small peak at −161 ppm indicated that some of the CH_3 groups were substituted by fluorine. Fluorine substitution tends to increase the reactivity of C−Si bonds (reactivity: $SiF_3 > SiF_2R > SiFR_2$).[24,25]

Scheme 3. Synthesis of PPDMVS, PFDMVS, and PVA



Oxidation Reactions. The oxidative cleavage of the PFDMVS carbon−silicon bonds was surprisingly difficult compared to that of low-MW organic fluorosilanes that are easily oxidized by various oxidants.[22,23,25] Thus the procedures demonstrated by Tamao[27] (Scheme 3) were unsuccessful. Even after refluxing PFDMVS with 14 mL of 30% H_2O_2 in MeOH/THF containing 10% KOH at 50 °C for 19 h, no oxidation of the starting polymer could be detected. The use of solvents such as ethylene glycol, diethyl ether, ethoxyethanol, and dioxane capable of dissolving the reactants, the use of higher temperatures (87 °C), and longer reaction times (19−23 h) did not result in a water-soluble polymer. A similar lack of reactivity is observed in many reactions carried out on macromolecules. Conceivably the use of stronger oxidants and more vigorous reaction conditions eventually will allow the quantitative oxidation of PFDMVS to poly(vinyl alcohol).

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